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THE VISIBLE EMISSION SPECTRUM OF BiCl MOLECULE

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(*Received August* 17, 1964; *Resubmitted November* 1964)

PLATE 1

ABSTRACT. The spectrum of BiCl was reinvestigated in a high frequency discharge both under low and high dispersion. A new system of 12 bands degraded to red designated an A'—X system has been observed and analysed in the region λ 4220–4000Å. The approximate vibrational constants were determined for the upper state of this system. The rotational analysis of (2,0, (3,0) and (4,0) bands of the A—X system of BiCl has led to the determination of the rotational constants. The bands appears to arise from a case (c)0^+—0^+ as was assumed previously by Khanna (1961).

INTRODUCTION

Two discrete band systems, one in the region λ5400–λ4220 Å and the other lying in the region λ4000--λ3600 Å were analysed and attributed to BiCl molecule. A summary of the early work on this molecule can be found in a paper recently published by Venkateswarlu and Khanna (1960). The vibrational analysis of the visible system was considerably extended to include many new bands in the region λ6170—λ4220 Å. From a rotational analysis of five bands (0, 2), (0, 3), (0, 4), (1, 2) and (1, 1) of this system, they have suggested that the system arises from a case (C) $0^+ - 0^+$ transition. The visible emission spectrum of BiCl has been investigated by the authors both under low and high dispersion. A new system of bands in the region λ4220—λ4000 has been observed and analysed. The rotational structure of (2, 0), (3, 0) and (4,0) has been examined in the second order of a 21 ft. concave grating spectrograph having dispersion (1.25 Å/mm), with the object of gaining new information of the rotational constants of the $v' = 2, 3, 4$ levels of the upper state and $v'' = 0$ level of the lower state of the visible system. The results of the rotational analysis of those three bands and the vibrational analysis of the system (A'—X) of bands in the region λ4220—λ4000 Å are presented in this paper.

EXPERIMENTAL

The spectrum was excited in a high frequency discharge through the vapour of anhydrous $BiCl_3$ under low pressure conditions. Photographs of the spectra in the visible region were taken on a Hilger 3 prism glass Littrow spectrograph

and in the second order of 21 ft. concave grating spectrograph using Agfa Super Special plates. Exposure of one hour's duration was found sufficient for developing the rotational structure of the visible system. The bands (2, 0), (3, 0) and (4, 0) which were found to be free from overlapping of neighbouring bands, were selected for measurement of the rotational lines. Further these bands are not previously analysed by Khanna (*loc. cit.*). A new group of bands in the region $\lambda 4220 - \lambda 4000$ Å degraded towards the red were measured from the plates taken on the glass littrow instrument. The accuracy of the measurements of the band heads is 2 cm^{-1} while that of the rotational lines is 0.07 cm^{-1}.

VIBRATIONAL ANALYSIS

Photographs of the spectra reveal the wellknown visible system of BiCl in the region $\lambda 6170 - \lambda 4220$ Å. In the region $\lambda 4220 - \lambda 4000$ a new group of bands degraded towards the longer wavelengths. These do not appear to be related in any way to the bands of the B–X system ($\lambda 4000 - \lambda 3600$). The bands of the B–X system were not observed in the source of excitation employed in the present work. The new bands in the region $\lambda 4220 - \lambda 4000$ Å could not also be fitted into the vibrational scheme of the A–X system analysed by Venkateswarlu and Khanna (*loc. cit.*). The bands appear therefore to constitute a new system of BiCl and can be seen in Fig. 1. The analysis of this system was greatly facilitated by the identification of a long v' progression with $v'' = 0$ and short v' progression with $v'' = 1$. The $\Delta G_{\frac{1}{2}}$ interval of the levels $v'' = 0$ and $v'' = 1$ agrees very closely with the corresponding interval of the ground state 'X' of BiCl. Thus the analysis confirms that the emitter of this system is diatomic BiCl. The two v' progressions of this new system designated as $A' - X$ are shown in Fig. 1. The bands of this system are too weak for a study of the rotational structure on the 21 ft. concave grating spectrograph. Table I gives the vibrational assignments and wave

TABLE I

Vibrational assignments and wave number data of $A' - X$ system of BiCl

v', v''	Wave number in Cm^{-1}
0,1	23321.0
1,1	23513.0
0,0	23628.0
2,1	23700.0
1,0	23817.0
2,0	24006.0
3,0	24188.0
4,0	24369.0
5,0	24538.0
6,0	24703.0
7,0	24860.0
8,0	25006.0

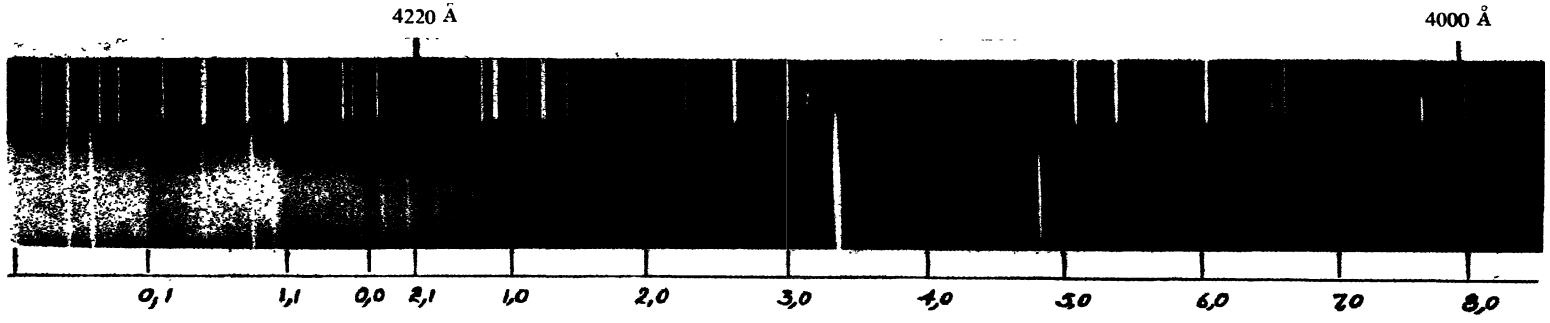

Fig. 1.—Emission Spectrum of $A\ ^1\Pi - X$ System of BiCl.

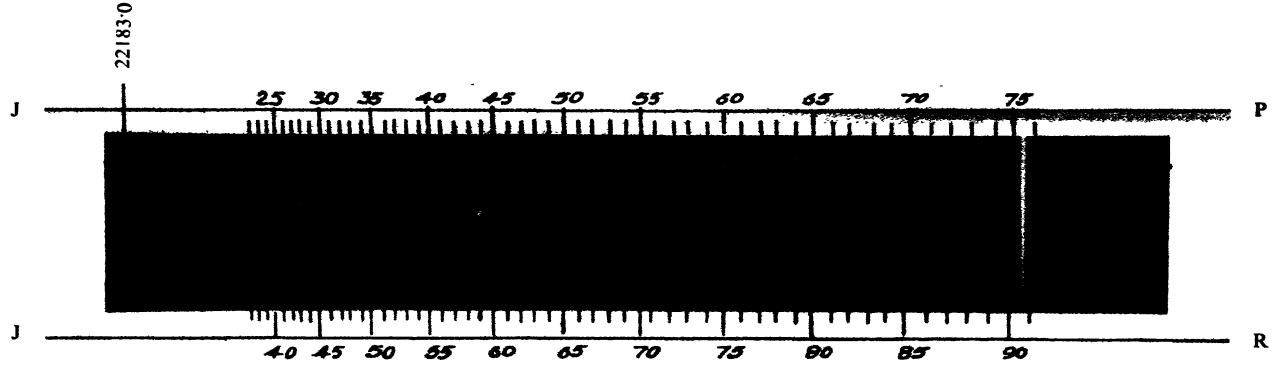

Fig. 2.—Rotational Structure of 2.0 band of $A—X$ system of BiCl.

number and Table II gives the vibrational scheme of R heads of the $A' - X$ system. Approximate vibrational constants were determined from the vibrational analysis of the $A' - X$ system of BiCl. They are $\omega'_e = 193.67$ cm^{-1} and $x'_e\omega'_e = 3.17$ cm^{-1}. From the magnitude of the vibrational constants of A and A' levels it may be concluded that they arise from the same electron configuration.

TABLE II

Vibrational analysis of $A'-X$ system of BiCl

v' \ v''	0		1
0	23628.0	307	23321.0
	189		192
1	23817.0	304	23513.0
	189		187
2	24006.0	306	23700.0
	182		
3	24188.0		
	181		
4	24369.0		
	169		
5	24538.0		
	165		
6	24703.0		
	157		
7	24860.0		
	147		
8	25006.0		

ROTATIONAL ANALYSIS

Khanna (1961) reported the rotational analysis and rotational constants of the upper and lower state of (0, 2), (0, 3), (0, 4) (1, 2) and (1,1) bands. From considerations of electronic configurations for the ground and first excited states of BiCl, the observed simplicity of the bands consisting of only P and R branches was attributed to a case (c) $0^+ - 0^+$ transition. Since the information about the rotational constants of the $v'' = 0$ and $v' = 2, 3, 4$ is still incomplete, the rotational analysis of the (2, 0), (3, 0) and (4, 0) bands have been carried by the authors. Each of these bands is found to consist of only two branches P and R, the branch that forms the head and which becomes weaker at high J values, is easily identified as R branch. It is observed that the P and R branches are resolved only at high J values as in the case of each of the five bands analysed by Khanna. As the lines of P and R branches do not show any sign of doubling even at high J values, it is assumed that the bands arise from a, case (c) $0^+ - 0^+$ transition.[1]

The procedure for the determination of J numbering of the rotational lines of five incompletely resolved bands of BiCl has been discussed in detail by

Khanna in his paper. The J numbering of the rotational lines of (2, 0), (3, 0) and (4,0) bands has been fixed in the usual way by comparison of the lower stato combination differences. The rotational lines of the P and R branches of (2, 0) band are shown in Fig. 2. The vacuum wave numbers and rotational assignment of (2, 0) (3, 0) and (4, 0) bands are given in Table III.

TABLE III

Vacuum wave-numbers and rotational assignments for (2, 0), (3, 0) and (4, 0) bands of $A-X$ system of BiCl

J	(2,0)		(3,0)		(4,0)	
	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$
20						
21						
22		22169.46				
23		168.55				
24		167.72				
25		166.84				
26		165.90				
27		165.01				
28		164.10				22570.28
29		163.16				569.24
30		162.07				568.22
31		160.99				567.24
32		159.91				566.17
33		158.78				565.08
34		157.69				563.91
35		156.42				562.80
36		155.30				561.65
37	22169.46	154.16				560.49
38	168.55	152.85				559.41
39	167.72	151.50				558.06
40	166.84	150.35				556.85
41	165.90	149.06				555.52
42	165.01	147.69				553.99
43	164.10	146.33			22570.28	552.74
44	22163.16	22144.88			22569.24	22551.39
45	162.07	143.43		22343.91	568.22	549.94
46	160.99	142.04		342.48	567.24	548.66
47	159.91	140.52		341.00	566.17	547.10
48	158.78	139.09		339.58	565.08	545.58
49	157.69	137.57		337.86	563.91	544.30
50	156.42	136.05		336.02	562.80	542.76
51	155.30	134.47		334.39	561.65	541.00
52	154.16	132.91		332.66	560.49	539.50
53	152.85	131.20		331.02	559.41	537.65
54	151.50	129.50		329.36	558.06	535.92
55	150.35	127.94		327.60	556.85	534.42
56	149.06	126.36		325.79	555.52	532.80
57	147.69	124.43		323.57	553.99	530.80
58	146.33	122.58		321.65	552.74	529.04
59	144.88	120.78	22343.91	319.80	551.39	527.22

TABLE III (*Contd.*)

J	(2,0)		(3,0)		(4,0)	
	R(*J*)	*P*(*J*)	*R*(*J*)	*P*(*J*)	*R*(*J*)	*P*(*J*)
60	143.43	119.00	342.48	317.88	549.94	525.41
61	142.04	117.03	341.00	315.91	548.66	523.58
62	140.52	115.10	339.58	313.96	547.10	521.61
63	139.09	113.22	337.86	311.96	545.58	519.65
64	137.57	111.24	336.02	309.90	544.30	517.78
65	136.05	109.49	334.39	307.90	542.76	515.93
66	134.47	107.47	332.66	305.74	541.00	513.79
67	132.91	105.57	331.02	303.60	539.50	511.87
68	131.20	103.11	329.36	301.50	537.65	509.75
69	129.53	101.11	327.60	299.27	535.92	507.63
70	22127.94	22099.01	22325.79	22297.00	22534.42	22505.56
71	126.36	096.82	323.97	294.86	532.80	503.39
72	124.43	094.72	322.16	292.63	530.80	501.30
73	122.58	092.54	320.30	290.24	529.04	499.09
74	120.78	090.23	318.35	287.93	527.68	496.82
75	119.00		316.36	285.61	526.03	494.36
76	117.03		314.40	283.24	524.11	492.26
77	115.10		312.36	280.84	522.25	490.05
78	113.22		310.44	278.34	520.32	487.74
79	111.24		308.38	275.96	518.40	485.21
80	109.49		306.35	273.52	516.44	482.79
81	107.47		304.25	270.87	514.52	480.42
82	105.57		302.16	268.37	512.55	
83	103.55		300.00	265.74	510.51	
84	101.59		297.81	263.16	508.47	
85	099.43		295.67		506.37	
86	097.36		293.39		504.39	
87	095.18		291.09		502.29	
88	092.98		288.83		500.02	
89	090.79		286.61		497.80	
90	088.63		284.29		495.52	
91	086.43		281.82		493.27	
92			279.46			
93			22276.96			
94			274.56			
95			271.96			
96			269.52			
97			267.08			
98			264.41			
99			261.69			
100						

The rotational constants of upper and lower states were determined from the relationship

$$\Delta_2 F(J) = 4B_v(J+1/2)$$

neglecting the effect of D correction term. The average value of $\Delta_2 F''(J)$ for (2, 0), (3, 0) and (4, 0) bands was used for determining the rotational constants

B_0''. Table IV summarises the rotational constants of various levels of the upper and lower states, including also the values obtained by Khanna (1961). The band origins obtained by plotting

$$R(J-1)+P(J) = 2\nu_0+2(B'-B'')J^2$$

against J^2 are also included in Table IV.

TABLE IV

Rotational constants of various levels of $A-X$ system of BiCl

Band Assignment	Band Head in cm^{-1}	$B_{v'}$ in cm^{-1}	$B_{v''}$ in cm^{-1}	Band Origin in cm^{-1}
2,0	22183.0	0.101_7	0.115_4	22181.2
3,0	22388.7	0.101_3	0.115_4	22386.8
4,0	22588.0	0.101_0	0.115_4	22586.3
*1,1	21666.0	0.102_1	0.114_6	21664.5
*1,2	21362.0	0.101_6	0.113_8	21360.3
*0,2	21147.0	0.102_5	0.114_4	21144.8
*0,3	20844.0	0.102_0	0.113_6	20842.0
*0,4	20543.0	0.101_3	0.112_6	20541.5

* Constants obtained by Khanna.

TABLE V

Rotational Constants of upper and lower states of $A-X$ system of BiCl

State	B_e cm^{-1}	α_e cm^{-1}	D_e cm^{-1}	β_e cm^{-1}	r_e Å	I_e 10^{-40} g cm^2
Upper	$.102_0$	—	—	—	2.349	274.3
Lower	$.115_4$	—	—	—	2.208	242.5

The r_e and I_e values for the upper and lower states are determined from the wellknown relations (Herzberg, 1950). The rotational constants of the upper and lower states are summarised in Table V. The D terms are not included in the table as they are too small to be determined with the accuracy of the present measurements.

The electronic transition of the $A-X$ system of BiCl has been fully discussed by Khanna and attributed to a case (c) 0^+-0^+ transition.

ACKNOWLEDGMENT

The authors wish to express their thanks to Prof. K. R. Rao for his interest and encouragement throughout the progress of this work. One of the authors (V. S. N. Rao) is grateful to the C.S.I.R. for the award of Junior Research Assistantship.

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